Development of a Total Beryllium Field Analyzer

Amy Ekechukwu, Paula Cable-Dunlap, Scott McWhorter, Charles Shick, Jr., Jeff Degange,

Executive Summary

- SRS assembled cross-division team to address Be analyses and digestion
- Need for Be field analysis compliant with 10 CFR 850 (real-time and near-real-time)
- SRS Field deployable analyzer - combines digestion method with colorimetric analysis

Why is Beryllium Important?

- Beryllium inhalation can result in development of Chronic Beryllium Disease (CBD)
- Several DOE sites have beryllium melting, casting, grinding, and machining operations (past or current)
- The DOE Beryllium Rule (10 CFR Part 850) established free-release limit of removable Be surface contamination at 0.2 micrograms per 100 cm^2

Be Analysis: Standard Protocol

- **Sample Digestion**
  - **Nitric acid (7300); nitric/sulfuric (7102)**
- **Analysis**
  - **Usually Inductively coupled plasma emission spectrometric (ICP-ES) analysis (7300)**
  - **Mass Spec (ICP-MS) , Atomic Absorbtion (GFAA) (7102) also used**
- **Laboratory analyses - turnaround time days to weeks**
- **Need for real-time or near-real-time method**

Be Field Analyzer Development

- SRS Be Team addressing method improvements
  - robust sample digestion for BeO
  - alternative analytical methods
    - colorimetric technique
- Field Analyzer - combines digestion method and colorimetric method into field portable instrument

Requirements for Field Analyzer

- Able to measure all forms of Be (oxide, metal)
- Meet free-release detection limit (0.2 μg/swipe)
- Portable
- Results at or near real-time
- Easy to manage wastes
- Simple and rugged

SRS Field Analyzer

- Combines digestion and colorimetric method
- Cost-effective
  - 75% cost reduction estimate
- Relatively short turnaround time
  - hours versus days
- Provides low detection limits required in DOE Be Rule
- Measures all forms of beryllium

Sample Digestion - Why?

- Formation of highly insoluble BeO can occur in DOE Be processes
- Standard NIOSH method (7300) does not address oxide (BeO)
- For “total” beryllium measurement, all Be must be in solution
- Sample matrix - Ghostwipe™ swipes (Environmental Express)

Typical Ghostwipe Swipe

ICP-MS Analysis of Machine Shop Swipe Matrix

Swipe Matrix Composition

Element	SQ Standard Known Concen. (ppb)	SQ Standard Measured Concen. (ppb)	Blank Swipe (µg/swipe)	Swipe Matrix (µg/swipe)
Li		0.0038	0.016	0.93
Be	100	100	<0.0004	0.014
B		0.24	1.2	34
Na		3	600	940
Mg	100	100	125	310
Al		1.9	3.5	16000
Sc		0.11	0.20	1.9
Ti		0.16	0.33	21
V		0.018	0.032	120
Cr		0.25	0.6	10000
Mn		0.24	0.29	1000
Fe		41	11	51000
Co	100	97	0.024	250
Ni	100	100	0.55	3400
Cu		0.9	1.8	7500
Zn		0.28	9.5	170
Ga		0.017	0.035	6.6
Sr		0.013	0.14	7.3
Y		0.005	0.0018	0.21
Zr		0.0098	0.05	1.4
Nb		<0.002	0.0018	7.4
Mo		0.1	0.15	460
Ru		<0.0098	<0.0005	4
Pd		<0.0097	0.0043	4.2
Ag		<0.004	0.027	3.5
Cd		<0.022	0.26	2.1
In	100	100	0.39	13
Sn		0.02	0.13	45
Sb		<0.0081	0.07	3.5
Ba		0.025	0.46	29
Ce	100	100	0.0047	0.76
Ta		<0.001	0.0017	0.63
W		0.45	0.39	520
Re		<0.0028	0.015	0.43
Au		<0.002	0.0011	0.13
Pb	100	100	1.3	55
Bi	100	100	0.018	1.5
U	100	100	0.016	0.14

Key Matrix Components

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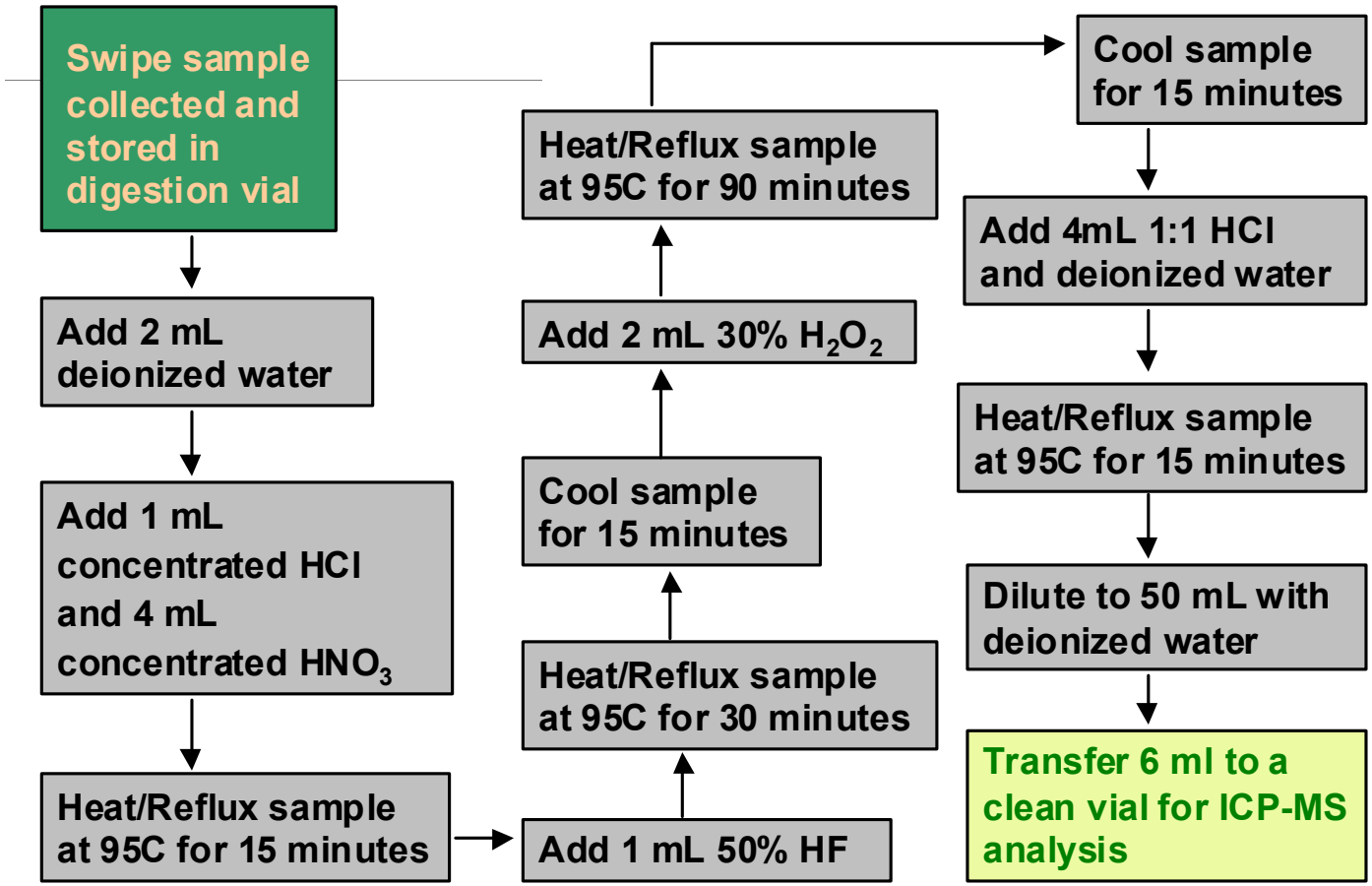
Digestion Methods Evaluated

- Multiple digestion protocols tested
- Fired Be-oxide particularly difficult to digest
- Most promising digestion involves HNO_3, HCl, HF, H_2O_2, Heating

EPA Modified 3050B Digestion



Colorimetric Method - 3 Stages

- SRTC modified LANL colorimetric wipe method
- Developed semi-quantitative liquid technique
- Used spectroscopy, enhanced chemistry to obtain linear results at required detection limit

Stage 1 - Modified Swipe Method

- LANL Method - Treated swipes with reagents, wiped surface, observe color
- SRS - Used same chemistry
  - wiped surface with clean wipe
  - add EDTA - Complex metals
  - buffer to pH 9-10 - Make Be available for reagent
  - add color reagent, Chromium Azurol S (CAS) and observed color change
- Could not meet free-release criteria

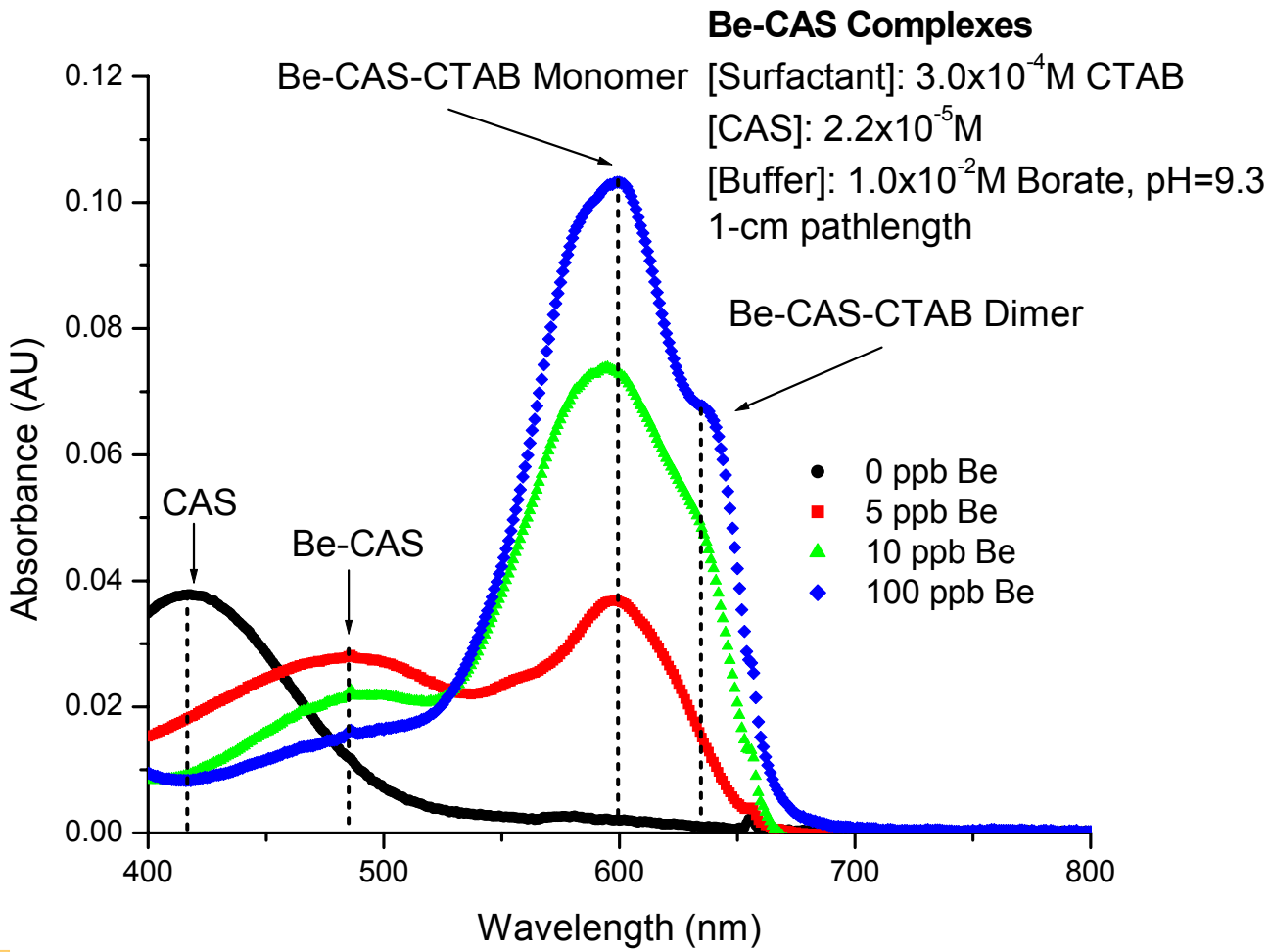
Stage 2 - Colorimetric Method

- Swipe surface
- Wash swipe with acid to solublize Be
- Perform chemistry on acid wash of swipe
- Observe color of liquid - positive visible result at 1 ug/swipe
- CAS (red) interfered with visible detection of CAS-Be (purple) complex at necessary detection limit (0.2 ug/swipe)

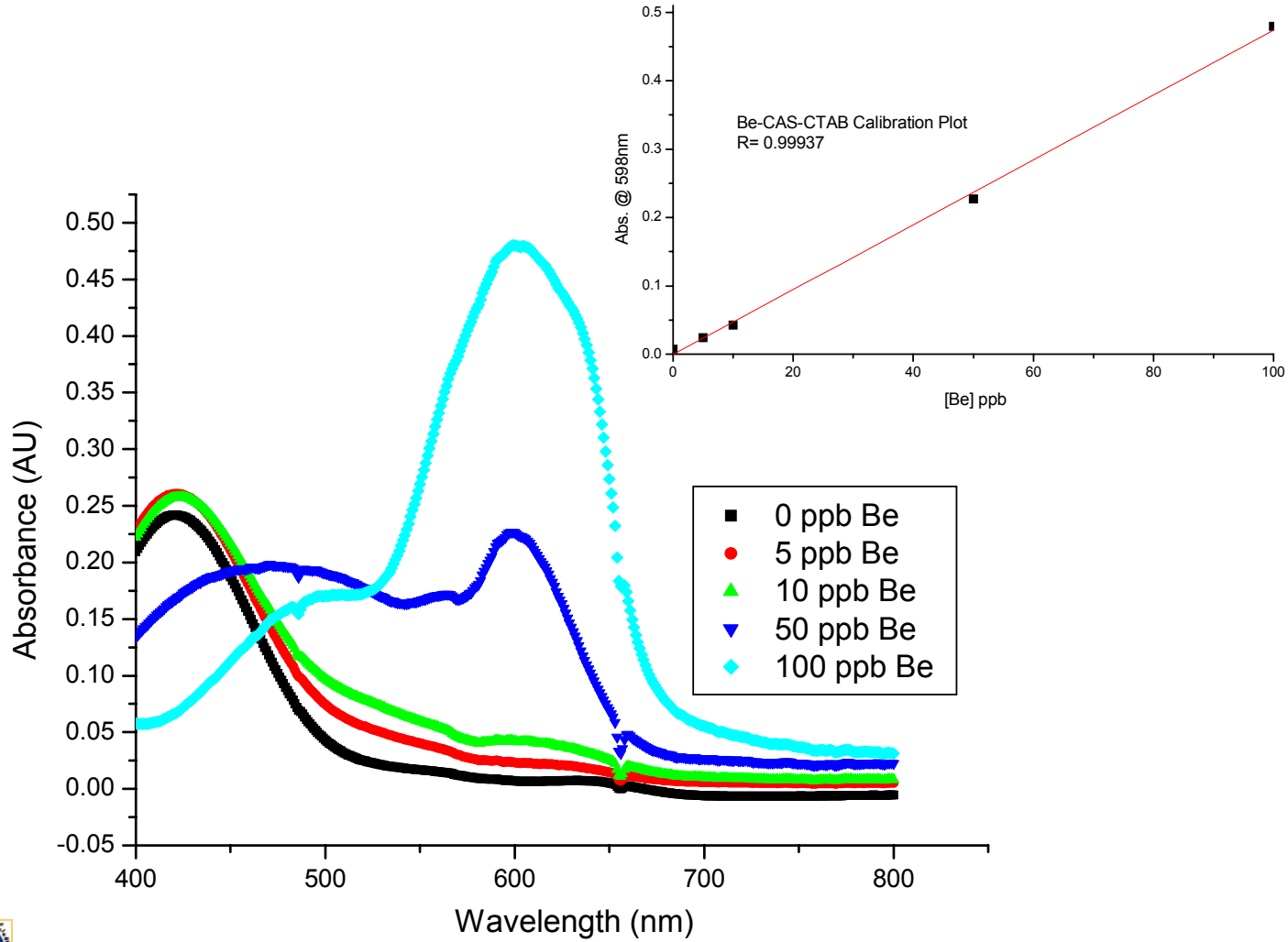
Stage 3 - Absorbance Method

- Needed to lower detection limits to 0.2 ug/swipe
- Used spectrophotometer
  - wash Be off of swipe and react with colorimetric reagent
  - measure absorbance.
- Addition of complexing agent to shift CAS-Be absorbance away from CAS absorbance

Initial Calibration Plot



Be-CAS-CTAB Optimized Calibration



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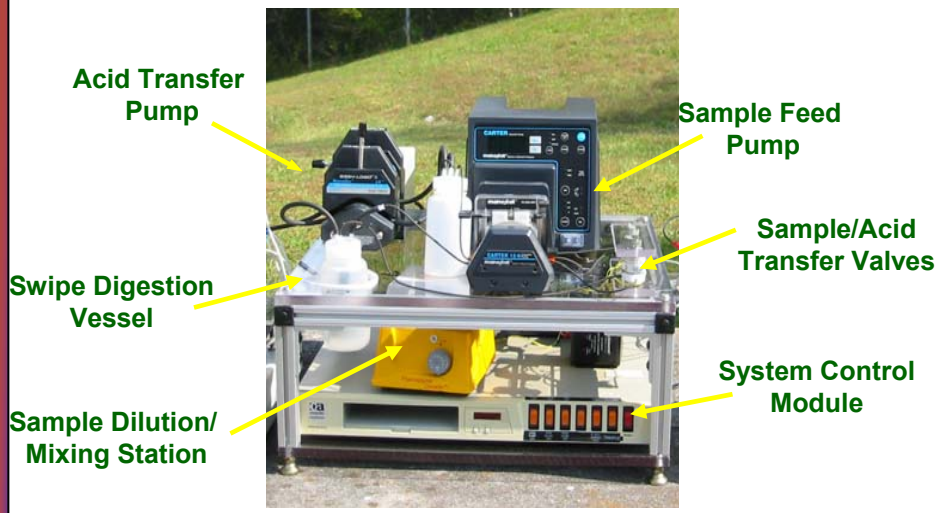
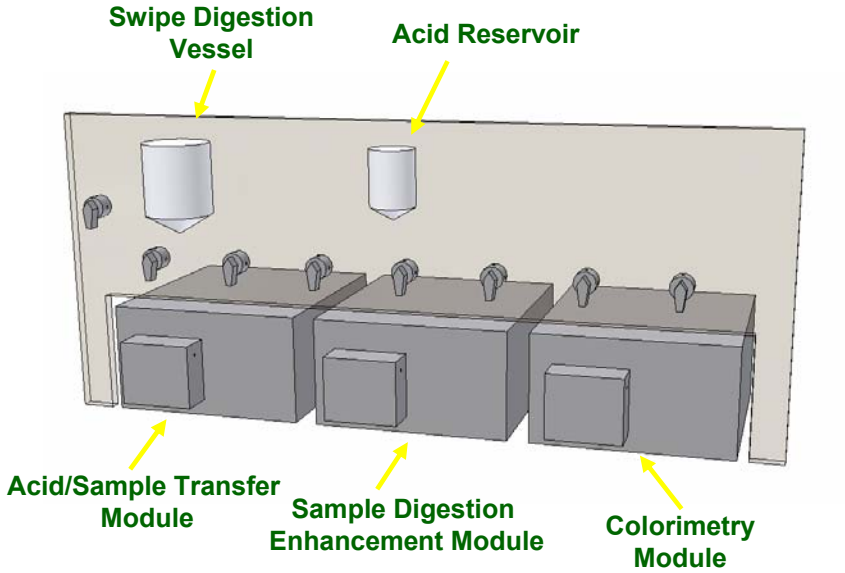
On-Line Swipe Digestion and Colorimetry (OSDAC) Interface

Proof of Concept Device



- On-line swipe digestion
- Automated sample transfer to dilution/ mixing station then to analyzer
- Separate control for acid flush of transfer lines to avoid sample cross-contamination

Fieldable OSDAC

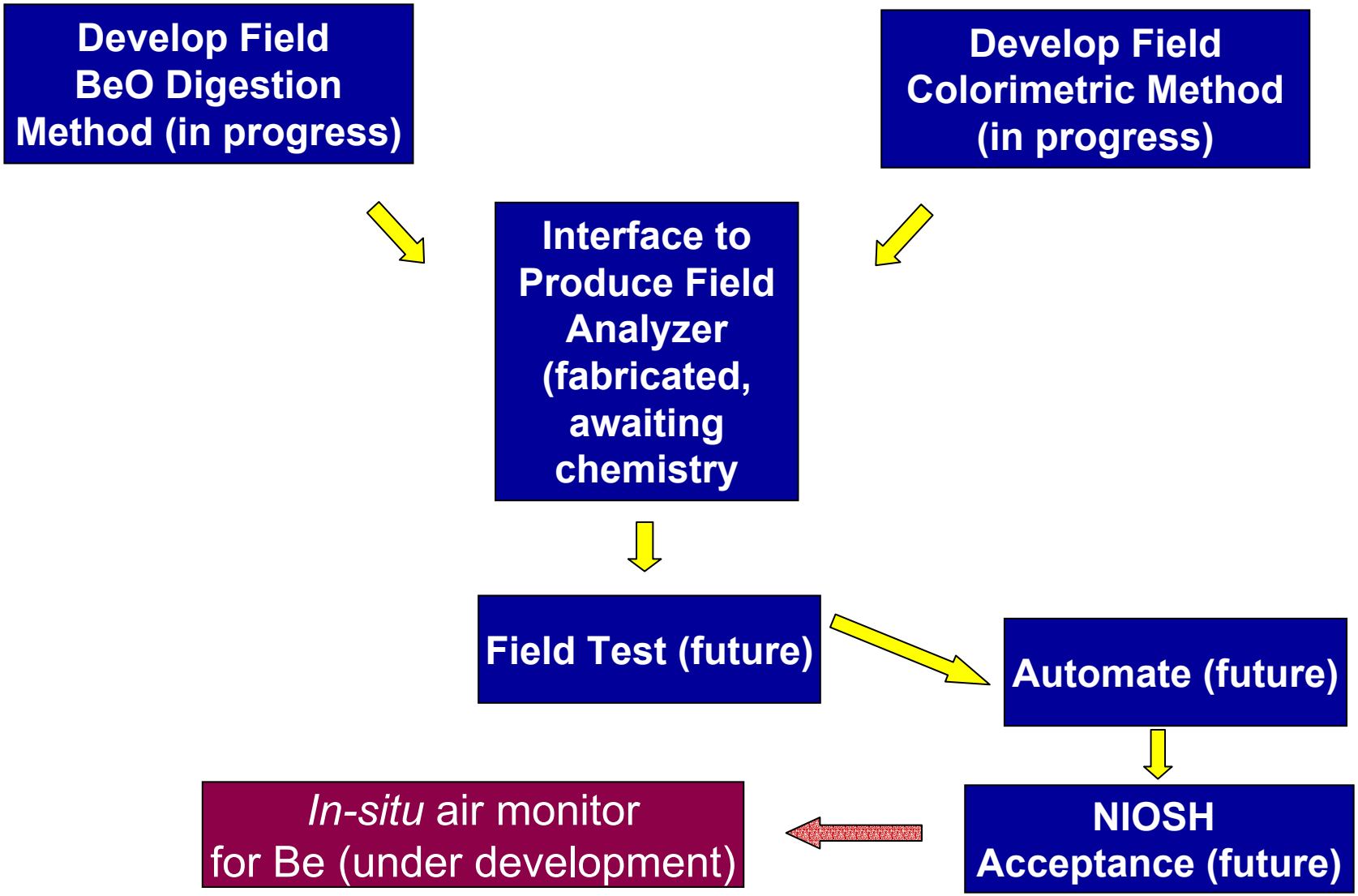


- Fully automated, integrated swipe digestion, sample transfer and analysis
- User friendly operation
- Robust, compact, lightweight
- Modular to prevent sample cross contamination

Planned Tasks

- Test digestion method on high fired Be-oxide - Fired Be-oxide being prepared for testing
- Decrease digestion time
- Test colorimetry on matrix matched samples containing interfering metals
- Test field analyzer using digestion and colorimetric chemistry

Path Forward



Digestion Methods Under Evaluation

- Y-12 - H_2O_2, Conc. H_2SO_4, microwave
- 3050B - HNO_3, H_2O_2, H_2SO_4
- 3050B Modified - HNO_3, HCl, HF, H_2O_2, Dilute HCl
- HNO_3, sonication
- HNO_3 , H_2SO_4 , HF
- HCl, $CuSO_4$, sonication, heat (10 min.), 3:1 HNO_3:H_2SO_4 , 2:1 HNO_3: HF

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